

Kramers turnover in class of thermodynamically open systems: Effect of interplay of nonlinearity and noises

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Abstract

A system-reservoir nonlinear coupling model has been proposed for a situation where the reservoir is nonlinearly driven by an external Gaussian stationary noise which exposes the system particles to a nonequilibrium environment. Apart from the internal thermal noise, the thermodynamically open system encounters two other noises that are multiplicative in nature. Langevin equation derived from the resulting composite system contains the essential features of the interplay between these noise processes. Based on the numerical simulation of the full model potential, we show that one can recover the turnover features of the Kramers dynamics even when the reservoir is modulated nonlinearly by an external noise.

1. Introduction

Inspired by a work of Christiansen [1], where a chemical reaction was considered as a diffusion problem, Kramers [2] introduced a Brownian motion model in a one-dimensional (along the reaction coordinate) force field to predict the existence of several kinetic regimes depending on the magnitude of the friction (very low or energy diffusion regime, and moderate to high or spatial diffusion regime). A clear understanding of the pre-factor of the Kramers equation is useful not only for completeness of the theory of escape rate, but also for explaining various phenomena. Therefore, for the last few decades, much effort has been put into extending the Kramers model [3, 4, 5, 6, 7, 8, 9]. Many authors have devised methods for obtaining escape rate in the whole range of friction by extending the basic assumptions found in the original Kramers work, known as the Kramers turnover problem [4, 5, 6, 10, 11]. Kramers has shown that the rate constant is proportional to γ (dissipation constant) when γ is low and proportional to γ^{-1} when γ is high. It can thus be expected that the value of the rate constant reaches a maximum at an intermediate γ and decreases to zero when γ approaches either zero or infinity. This dependence of the rate constant on friction is known as Kramers turnover. However, Kramers could not derive a uniform expression for the rate, valid for all values of the friction coefficient. In fact, analytical solutions for Kramers equation are only possible for very simple interaction models [3, 4, 6]. The systematic solution of the Kramers turnover problem for the thermodynamically closed system was given by Pollak–Grabert–Hänggi(PGH) [12] (one of the foremost studies about

turnover) who generalized the Kramers model to an arbitrary time-dependent friction and demonstrated that the turnover formula due to Mel’nikov and Meshkov [5, 13] can be obtained without any *ad hoc* bridging. Later, the PGH theory was generalized to many dimensions [14, 15].

Activated rate processes in one-dimensional surface diffusion have been studied by Pollak *et al.* [14, 16]. Hershkovitz and Pollak [15] studied the length dependence of the classical activated transfer rate across a bridge and found that the Kramers turnover theory in the rate suffices for understanding the bridge length and friction dependence of the rate. Rips and Pollak [17] extended the PGH method in the context of quantum Kramers turnover problem. Segal *et al.* [18] have provided the first analysis of the transition from the tunnelling to the thermally activated regime in a variant of the quantum Kramers problem as a function of the barrier length. Vega *et al.* [19] have studied the Kramers turnover theory in activated atom-surface diffusion using mean first passage time. Shepherd and Hernandez [20, 21, 22] have exploited the mean first passage time (MFPT) based rate formula to analyze the interplay between Kramers turnover and resonant activation for the escape rates on stochastic bistable and aperiodic potentials. The development in Ref. [22] is particularly interesting as it investigates the low friction regime (the most difficult part of Kramers turnover theory to illustrate) in conjunction with stochastic aperiodic potentials. Recently, Kramers turnover has also been realized during the investigation of the forward and backward reaction rates of the $\text{LiNC} \rightleftharpoons \text{LiCN}$ isomerization reaction in a bath of argon atoms at various densities using molecular dynamics simulations due to García-Müller *et al.* [23]. Their work provides clear evidence for the increase in rates with microscopic friction in the energy-diffusion regime in chemical system.

The last few decades have observed a crescendo of research activity in the field of nonequilibrium statistical mechanics us-

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ing the system-reservoir (SR) model [24, 25]. In the overwhelming majority of situations, the interaction between the system and the reservoir has been considered to be linear in both co-ordinates as well system co-ordinates. This in turn relates the additive noise of the thermal bath with linear dissipation of the system through fluctuation–dissipation relation (FDR). On the other hand, if the SR coupling is nonlinear in system coordinate, the corresponding Hamiltonian gives rise to a Langevin equation with state-dependent dissipation and internal multiplicative thermal noise. As the total SR combination is thermodynamically closed, the energy balance condition again is reflected through FDR [26]. If density of bath modes is such that the associated noise is stationary and Gaussian, one can numerically solve the associated Langevin equation for barrier crossing dynamics to observe the turnover phenomena. It should be recognized that it is very hard to obtain a simple expression for escape rate, even for a white noise process, when the dissipation is state dependent and the noise process is multiplicative in nature. Consequently, PGH [12]-type analysis for turnover problem is very hard to achieve in such cases [23]. At this point, one might wonder if the turnover phenomena can be observed when the SR combination is thermodynamically open and hence there is no energy-balance relation like FDR.

Among many other situations, the SR combination will be thermodynamically open if one drives the system externally (keeping the reservoir in thermal equilibrium). On the other hand, in spite of direct driving, one may expose the reservoir to an external modulation. A number of different situations depicting the modulation of the bath by an external noise may be physically relevant [27, 28, 29, 30]. Whether the system or the reservoir is driven by an external noise, there is an additional mechanism to inject energy into the system and clearly, there is no FDR in such a situation. Inspection of any such situation may be relevant to examine the turnover phenomena in the rate. In what follows, we address the later situation where the reservoir is modulated externally by a random force to make the SR combination thermodynamically open. It is our aim here to search for the signature of Kramers turnover in the rate, emerging from the nonlinear driving of the bath by an external noise. The effect of nonlinear modulation of the reservoir by an external agency is considered indispensable in explaining the phenomena of activation of a quasibound species (reactants surrounded by the solvent molecules) above its trapping potential in the presence of high intensity light sources. For example, one may consider an isomerization reaction ($A \rightleftharpoons B$) in a photochemically active solvent in the presence of an external light source with high intensity.

2. Methodology

To start with, we consider a classical particle of unit mass being coupled to a heat bath consisting of N -mass weighted harmonic oscillators, characterized by the frequency set $\{\omega_j\}$ (i.e. the bath degrees of freedom are described by an ensemble of oscillators). In addition to that, the heat bath is nonlinearly driven by an external noise identified as $\epsilon(t)$. The Hamiltonian

for the composite system is

$$H = H_S + H_B + H_{SB} + H_{\text{int}} \quad (1)$$

where the Hamiltonian of the system is expressed as: $H_S = (p^2/2) + V(q)$ with $V(q)$ being the potential energy function and p and q being respectively the coordinate and the momentum of the system particle. $H_B + H_{SB} = \sum_{j=1}^N \left[\frac{p_j^2}{2} + \frac{1}{2} \omega_j^2 \{x_j - c_j f(q)\}^2 \right]$ where $\{x_j, p_j\}$ are the variables for the j -th bath oscillator. The system-heat bath interaction is given by the coupling term $c_j \omega_j f(q)$ where c_j is the coupling strength and $f(q)$ is some well-behaved function of the system coordinate q only. Through the insertion of the term $f(q)$, we have considered the SR interaction to be, in general, nonlinear. For bilinear system-bath coupling, $f(q)$ would have been taken as some linear function of q . The interaction between the heat bath and external noise $\epsilon(t)$ is taken as $H_{\text{int}} = \sum_{j=1}^N \kappa_j g(x_j) \epsilon(t)$ where κ_j denotes the strength of the interaction and $g(x_j)$ is an arbitrary analytic function of the bath variable x_j . This type of interaction makes the bath variables explicitly time dependent. A large class of phenomenologically modelled stochastic differential equations may be obtained from a microscopic Hamiltonian for a particular choice of coupling function $g(x_j)$ and have already been used for microscopic realization of Kubo-type oscillator and correlated noise processes [31, 32]. If one chooses, for example, $g(x_j) = \frac{1}{2} x_j^2$, the spring constants of the bath oscillators become fluctuating. In what follows, we choose $g(x_j) = x_j + \frac{1}{2} x_j^2$; a linear-linear(LL) and a square-linear(SL) coupling between the noise and bath variables. Recently, the effect of such LL coupling and SL coupling between the system and the reservoir have been studied by Tanimura and coworkers[33] in the context of spectroscopic studies. The notation of the hierarchical representation of the underlying Hamiltonian system in Eq.(1) and its subsequent analytic representations in extended Langevin equations has been discussed by Popov and Hernandez [34].

In what follows the external noise $\epsilon(t)$ is taken to be stationary, Gaussian with statistical properties $\langle \epsilon(t) \rangle_e = 0$

$$\langle \epsilon(t) \epsilon(t') \rangle_e = \psi(t - t') = \frac{D_\epsilon}{\tau_\epsilon} \exp\left(-\frac{|t - t'|}{\tau_\epsilon}\right), \quad (2)$$

where D_ϵ is the strength of the noise and τ_ϵ is its correlation time. For $\tau_\epsilon \rightarrow 0$, $\epsilon(t)$ becomes δ -correlated with statistical property: $\langle \epsilon(t) \epsilon(t') \rangle_e = 2D_\epsilon \delta(t - t')$. In Eq.(2), $\langle \cdots \rangle_e$ implies averaging over the external noise processes. In this context, we want to mention that the presence of noise and nonlinearity are unavoidable in general physical systems. So, one must take into account the interplay between these two factors on the dynamics of the system.

From Eq. (1), we have the dynamical equations for the system and the bath variables as

$$\ddot{q}(t) = -V'(q(t)) + f'(q(t)) \sum_j c_j \omega_j^2 \{x_j(t) - c_j f(q(t))\}, \quad (3)$$

$$\ddot{x}_j(t) + \{\omega_j^2 + \kappa_j \epsilon(t)\} x_j(t) = -\kappa_j \epsilon(t) + c_j \omega_j^2 f(q(t)). \quad (4)$$

To solve Eq.(4) for $x_j(t)$, we assume a solution of the form

$$x_j(t) = x_j^0(t) + \kappa_j x_j^1(t), \quad (5)$$

where $x_j^0(t)$ is the solution of the unperturbed equation of motion (EOM)

$$\ddot{x}_j^0(t) + \omega_j^2 x_j^0(t) = c_j \omega_j^2 f(q(t)). \quad (6)$$

We now consider that at $t = 0$, the heat bath is in thermal equilibrium in the presence of the system but in the absence of the external noise $\epsilon(t)$. Subsequently, at $t = 0_+$, the external noise agency is switched on and the heat bath is modulated by $\epsilon(t)$. Then $x_j^1(t)$ must satisfy the equation

$$\ddot{x}_j^1(t) + \omega_j^2 x_j^1(t) = -\epsilon(t) - \epsilon(t)x_j^0(t). \quad (7)$$

with the initial conditions $x_j^1(0) = p_j^1(0) = 0$. Now, the solution of Eq.(7) is given by

$$\begin{aligned} x_j^1(t) &= -\frac{1}{\omega_j} \int_0^t dt' \sin \omega_j(t-t') \epsilon(t') \\ &\quad - \frac{1}{\omega_j} \int_0^t dt' \sin \omega_j(t-t') x_j^0(t') \epsilon(t'). \end{aligned} \quad (8)$$

The formal solution of Eq.(6) is given by

$$\begin{aligned} x_j^0(t) &= x_j^0(0) \cos \omega_j(t) + \frac{p_j^0(0)}{\omega_j} \sin \omega_j(t) \\ &\quad + c_j \omega_j \int_0^t dt' \sin \omega_j(t-t') f(q(t')), \end{aligned} \quad (9)$$

where $x_j^0(0)$ and $p_j^0(0)$ are respectively the initial position and momentum of the j -th bath oscillator. Now, using this solution in Eq.(8), we have (after an integration by parts) the EOM for bath variables $x_j(t)$ [from Eq.(5)] as

$$\begin{aligned} x_j(t) - c_j f(q(t)) &= \left\{ x_j^0(0) - c_j f(q(0)) \right\} \cos \omega_j(t) \\ &\quad + \frac{p_j^0(0)}{\omega_j} \sin \omega_j(t) \\ &\quad - c_j \int_0^t dt' \cos \omega_j(t-t') f'(q(t')) \dot{q}(t') \\ &\quad - \frac{\kappa_j}{\omega_j} \int_0^t dt' \sin \omega_j(t-t') \epsilon(t') \\ &\quad - \frac{\kappa_j}{\omega_j} \int_0^t dt' \sin \omega_j(t-t') x_j^0(t') \epsilon(t'). \end{aligned} \quad (10)$$

Using the above solution in Eq.(3), we obtain the EOM for the system variables as

$$\begin{aligned} \ddot{q}(t) &= -V'(q(t)) - f'(q(t)) \int_0^t dt' \gamma(t-t') f'(q(t')) \dot{q}(t') \\ &\quad + f'(q(t)) F(t) + f'(q(t)) \pi(t) - f'(q(t)) \\ &\quad \times \int_0^t dt' \left\{ \sum_j c_j \kappa_j \omega_j \sin \omega_j(t-t') x_j^0(t') \right\} \epsilon(t'), \end{aligned} \quad (11)$$

where the damping kernel is given by $\gamma(t) = \sum_j c_j \omega_j^2 \cos \omega_j t$. $F(t)$ is the internal thermal noise generated through the coupling

between the system and the heat bath and is given by

$$\begin{aligned} F(t) &= \sum_j c_j \omega_j^2 \left[\left\{ x_j^0(0) - c_j f(q(0)) \right\} \cos \omega_j t \right. \\ &\quad \left. + \frac{p_j^0(0)}{\omega_j} \sin \omega_j t \right], \end{aligned} \quad (12)$$

and

$$\pi(t) = \int_0^t dt' \varphi(t-t') \epsilon(t'), \quad (13)$$

is a dressed noise that depends on the external noise $\epsilon(t)$ and

$$\varphi(t) = \sum_j c_j \kappa_j \omega_j \sin \omega_j t. \quad (14)$$

Clearly, the system does not encounter the external noise $\epsilon(t)$ directly, rather, the driving of the bath by the external noise $\epsilon(t)$ results in a dressed noise. The form of Eq.(11) therefore suggests that the system is driven by two forcing functions $F(t)$ and $\pi(t)$. $F(t)$ depends on the initial conditions of the bath oscillators for a fixed choice of the initial condition of the system degrees of freedom. To define the statistical properties of $F(t)$, we assume that the initial distribution is the one in which the bath is equilibrated at $t = 0$ in the presence of the system but in the absence of the external noise agency. Let us now digress a little bit about $\pi(t)$. The statistical properties of $\pi(t)$ are determined by the normal-mode density of the bath frequencies, the coupling of the system with the bath, the coupling of the bath with the external noise, and the external noise itself. Equation (13) is reminiscent of the familiar linear relation between the polarization and the external field, where π and ϵ play the role of the former and the latter, respectively. The function $\varphi(t)$, thus may be taken as the response function of the bath. The very structure of $\pi(t)$ suggests that this forcing function, although originating from an external force, is different from a direct driving force acting on the system. The distinction lies at the very nature of the bath characteristics (rather than system characteristics) as reflected in the relations Eqs. (13) and (14). At this point, we note that the forcing term $F(t)$ is deterministic. It ceases to be deterministic if it is not possible to specify all the $x_j^0(0)$'s and $p_j^0(0)$'s, i.e., the initial conditions of all the bath variables, exactly. The standard procedure to overcome this difficulty is to consider a distribution of $x_j^0(0)$ and $p_j^0(0)$ to specify the statistical properties of the bath-dependent forcing term $F(t)$. The distribution of the bath oscillators is assumed to be a canonical distribution of the Gaussian form

$$\begin{aligned} \rho_{\text{eq}}^{\text{bath}}(0) &= N \exp \left[-\frac{1}{k_B T} \left\{ \sum_j \left(\frac{p_j^{02}(0)}{2} \right. \right. \right. \\ &\quad \left. \left. + \frac{1}{2} \omega_j^2 (x_j^0(0) - c_j f(q(0)))^2 \right) \right\} \right], \end{aligned} \quad (15)$$

where N is the normalization constant. This choice of the distribution function of the bath variables makes the initial noise Gaussian. It is now easy to verify the statistical properties of $F(t)$ as $\langle F(t) \rangle = 0$ and $\langle F(t) F(t') \rangle = k_B T \gamma(t-t')$ where k_B

is the Boltzmann constant and T is the equilibrium temperature. Here, $\langle \cdots \rangle$ implies the average over the initial distribution given in Eq.(15). The second relation is the FDR [10] which ensures that the bath was in thermal equilibrium at $t = 0$, in presence of the system. To proceed further, we consider the last term of Eq.(11) as

$$\Gamma(t) = f'(q(t)) \int_0^t dt' \sum_j c_j \kappa_j \omega_j \sin \omega_j(t-t') \epsilon(t') x_j^0(t'). \quad (16)$$

We now put the expression for $x_j^0(t')$ from Eq.(9). The solution Eq.(9), consists of two parts, the homogeneous solution of Eq.(6) which is the free evolution of bath variables is the fast part. The second one is the solution of the corresponding inhomogeneous equation which gives the the forced oscillation expressed as $c_j \omega_j \int_0^t dt' \sin \omega_j(t-t') f(q(t'))$. As the fast part dies out quickly for damped driven oscillator, we pick the particular solution of Eq.(9) only for $x_j^0(t)$ and consequently, Eq.(11) becomes

$$\begin{aligned} \ddot{q}(t) = & -V'(q(t)) - f'(q(t)) \int_0^t dt' \gamma(t-t') f'(q(t')) \dot{q}(t') \\ & + f'(q(t)) F(t) + f'(q(t)) \pi(t) \\ & - f'(q(t)) \int_0^t dt' \epsilon(t') \int_0^{t'} dt'' f(q(t'')) \\ & \times \left\{ \sum_j c_j^2 \kappa_j \omega_j^2 \sin \omega_j(t-t') \sin \omega_j(t'-t'') \right\}. \end{aligned} \quad (17)$$

To identify Eq.(17) as a generalized Langevin equation, we must impose some conditions on the coupling coefficients c_j and κ_j , on the bath frequencies ω_j and on the number N of the bath oscillators that will ensure that $\gamma(t)$ is indeed dissipative and the last term in Eq.(17) is finite for $N \rightarrow \infty$. A sufficient condition for $\gamma(t)$ to be dissipative is that it is positive-definite and decreases monotonically with time. These conditions are achieved if $N \rightarrow \infty$ and if $c_j \omega_j^2$ and ω_j are sufficiently smooth functions of j [35]. As $N \rightarrow \infty$, one replaces the sum by an integral over ω weighted by a density of states $\rho(\omega)$. Thus, to obtain a finite result in the continuum limit, the coupling function $c_j = c(\omega)$ and $\kappa_j = \kappa(\omega)$ are chosen as $c(\omega) = \frac{c_0}{\omega \sqrt{\tau_c}}$ and $\kappa(\omega) = \kappa_0$ where c_0 and κ_0 are constants and τ_c is the correlation time of the heat bath. The choice $\kappa(\omega) = \kappa_0$ is the simplest one where we assume that every bath mode is excited with the same intensity. This simple choice makes the relevant term finite for $N \rightarrow \infty$. Consequently, $\gamma(t)$ becomes

$$\gamma(t) = \left(\frac{c_0^2}{\tau_c} \right) d\omega \rho(\omega) \cos \omega t, \quad (18)$$

where $1/\tau_c$ may be characterized as the cut-off frequency of bath oscillators. The density of modes of $\rho(\omega)$ of the heat bath is assumed to be Lorentzian,

$$\rho(\omega) = \left(\frac{2}{\pi} \right) \left[\frac{\omega^2}{\tau_c^{-2} + \omega^2} \right]. \quad (19)$$

This type of choice of $\rho(\omega)$ may be encountered in many situations in chemical physics and condensed matter physics[36,

37, 38, 39] and resembles broadly, in behavior, the hydrodynamic modes in certain macroscopic systems[40]. With these forms of $\rho(\omega)$, $c(\omega)$ and $\kappa(\omega)$, we have the expression for $\gamma(t)$ as $\gamma(t) = \frac{c_0^2}{\tau_c} \exp\left(-\frac{t}{\tau_c}\right)$ which reduces to $\gamma(t) = 2c_0^2 \delta(t) = 2\gamma \delta(t)$ for $\tau_c \rightarrow 0$ where $\gamma = c_0^2$ and is a Markovian dissipation constant and consequently, one obtains δ -correlated internal noise processes. With these forms of density of modes $\rho(\omega)$ and coupling functions, $c(\omega)$ and $\kappa(\omega)$, the response function $\varphi(t)$ can be written in the continuum limit as

$$\begin{aligned} \varphi(t) &= \int_0^\infty d\omega \rho(\omega) c(\omega) \kappa(\omega) \omega \sin \omega t \\ &= \frac{2}{\pi} c_0 \kappa_0 \frac{1}{\tau_c} \int_0^\infty d\omega \omega \frac{\sin \omega t}{\tau_c^{-2} + \omega^2} \\ &= \frac{c_0 \kappa_0}{\tau_c} \exp\left(-\frac{t}{\tau_c}\right). \end{aligned} \quad (20)$$

Clearly, for $\tau_c \rightarrow 0$, $\varphi(t)$ reduces to $\varphi(t) = 2c_0 \kappa_0 \delta(t)$. Now, using the standard trigonometric identity, the last term in Eq.(17) can be written as

$$\begin{aligned} \Delta(t) &= f'(q(t)) \left[\frac{1}{2} \int_0^t dt' \epsilon(t') \int_0^{t'} dt'' f[q(t'')] \right. \\ &\quad \times \sum_j c_j^2 \kappa_j \omega_j^2 \cos \omega_j(t-2t'+t'') \\ &\quad - \frac{1}{2} \int_0^t dt' \epsilon(t') \int_0^{t'} dt'' f[q(t'')] \\ &\quad \left. \times \sum_j c_j^2 \kappa_j \omega_j^2 \cos \omega_j(t-t') \right]. \end{aligned} \quad (21)$$

Now, using the assumed expressions for the coupling functions $c(\omega)$ and $\kappa(\omega)$ and the density of modes $\rho(\omega)$, one easily observes that the two sums in Eq.(21) may be approximated as a δ -function,

$$\begin{aligned} \sum_j c_j^2 \kappa_j \omega_j^2 \cos \omega_j(t+t''-2t') &= \int d\omega \rho(\omega) \{c(\omega)\}^2 \kappa(\omega) \\ &\quad \times \omega^2 \cos \omega(t+t''-2t') \\ &= 2c_0^2 \kappa_0 \delta(t+t''-2t') \end{aligned} \quad (22)$$

Similarly,

$$\sum_j c_j^2 \kappa_j \omega_j^2 \cos \omega_j(t-t'') = 2c_0^2 \kappa_0 \delta(t-t''). \quad (23)$$

Thus, in the continuum limit, the expression for $\Delta(t)$ reduces to

$$\begin{aligned} \Delta(t) &= c_0^2 \kappa_0 f'(q(t)) \left[\int_0^t dt' \epsilon(t') \int_0^{t'} dt'' f[q(t'')] \right. \\ &\quad \times \delta(t+t''-2t') \\ &\quad \left. - \int_0^t dt' \epsilon(t') \int_0^{t'} dt'' f[q(t'')] \delta(t-t'') \right]. \end{aligned} \quad (24)$$

With the property of δ -function, the first double integral in Eq.(24) may be written as

$$\begin{aligned} &\int_0^t dt' \epsilon(t') \int_0^{t'} dt'' f[q(t'')] \delta(t+t''-2t') \\ &= \frac{1}{2} \int_0^t dy \epsilon\left(\frac{y+t}{2}\right) f(q(y)). \end{aligned} \quad (25)$$

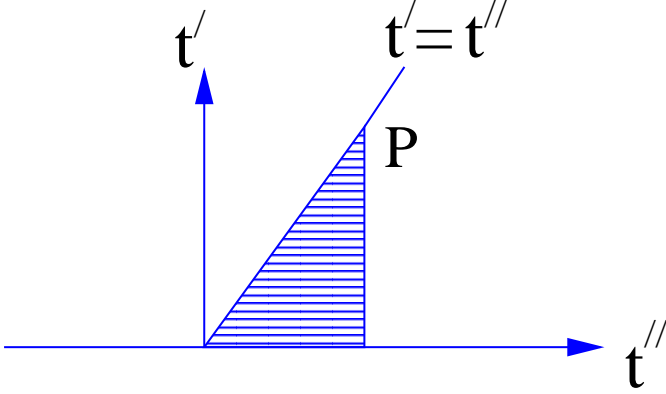


Figure 1: Domain of integration of $\int_0^t dt' \epsilon(t') \int_0^{t'} dt'' f[q(t'')] \delta(t - t')$ in Eq. (24).

As the system variable evolves much slowly in comparison to the external noise $\epsilon(t)$, the right hand side of Eq.(25) may be approximated as $\frac{1}{2} \left[\int_0^t dy \epsilon\left(\frac{y+t}{2}\right) \right] f(q(0))$. For large t , we note that as

$$\lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' \epsilon(t') = \langle \epsilon(t) \rangle_e = 0, \quad (26)$$

the first term in the expression of $\Delta(t)$ vanishes.

To perform the second integration; $\int_0^t dt' \epsilon(t') \int_0^{t'} dt'' f[q(t'')] \delta(t - t')$, we consider the region of integration, shown as the shaded triangle in Figure 1. From the property of δ -function, one observes that the above integral will contribute only when $t'' = t$ but the inequality $0 \leq t'' \leq t' \leq t$ demands that at the same time, t' should be equal to t . Thus, the contribution from the integral come out only at point P and the value of this contribution is $f(q(t))\epsilon(t)$. Using all the above facts, we obtain from Eq.(17) the EOM for system variables, in the limit $\tau_c \rightarrow 0$, as

$$\ddot{q}(t) = -V'(q(t)) - \gamma[f'(q)]^2 p + f'(q(t))F(t) + f'(q(t))\pi(t) + \gamma\kappa_0 f(q)f'(q)\epsilon(t). \quad (27)$$

This equation can be used to explore the distinctive aspects of the reservoir (driven nonlinearly by an external noise) modulated dynamics of the system in contrast to direct driving of the system by the external noise. This will help us to elucidate the special role of the reservoir response function in controlling the escape of a Brownian particle from the metastable state.

3. Results and Discussion: Kramers turnover

Before examining the noise induced transport, it is instructive here to have a close look at the above Langevin equation, where three noise processes appear and all these noise processes appear multiplicatively. $F(t)$ is the internal thermal noise for which FDR exists. $\pi(t)$ is the dressed noise and $\epsilon(t)$ is the external noise. Instead of nonlinear SR coupling, if one considers bilinear coupling, i.e., $f(q) = q$, the above equation Eq.(27) reads as

$$\ddot{q}(t) = -V'(q(t)) - \gamma p + F(t) + \pi(t) + \gamma\kappa_0 q\epsilon(t), \quad (28)$$

which indicates that both the thermal noise and dressed noise appear additively but the last noise containing term appears multiplicatively. The effect of interference of colored additive and multiplicative white noises on escape rate has also been explored using this type of equation[41]. Let us now discuss a little bit on the origin of the noises appeared in Eq.(28). $F(t)$, the usual thermal noise appears due to the system-bath interaction. The driving of the reservoir by external noise yields the last two terms in Eq.(28). If we choose the bath-noise coupling function $g(x_j)$ to be linear in bath variable, one will encounter the $\pi(t)$ noise in Eq.(28) only and the last term will disappear. On the other hand, if $g(x_j)$ be quadratic, i.e., $g(x_j) = (1/2)x_j^2$, $\pi(t)$ term disappears and the last term plays its role in the dynamics. Here, it is interesting to note that the multiplicative nature of the last noise process stems from the nonlinear driving of the bath but not from the nonlinearity of system-reservoir coupling function, which is the case for the other two noises. Here, we enunciate a system without proof that if the bath-noise coupling function be $g(x_j) = ax_j + bx_j^2 + cx_j^3 + \dots$, then for linear system reservoir coupling, the resulting Langevin equation will read as

$$\ddot{q}(t) = -V'(q(t)) - \gamma p + F(t) + \pi(t) + Bq\epsilon(t) + Cq^2\epsilon(t). \quad (29)$$

At this point, it is instructive to consider the statistical property of the dressed noise $\pi(t)$ which can be easily verified as $\langle \pi(t) \rangle_e = 0$ and

$$\langle \pi(t)\pi(t') \rangle_e = \int_0^t dt'' \int_0^{t'} dt''' \varphi(t - t'')\varphi(t' - t''') \times \psi(t'' - t'''). \quad (30)$$

If we assume that the external noise $\epsilon(t)$ is δ -correlated, i.e., $\langle \epsilon(t)\epsilon(t') \rangle = 2D_e\delta(t - t')$, then in the limit $\tau_c \rightarrow 0$, the correlation function of $\pi(t)$ becomes $\langle \pi(t)\pi(t') \rangle_e = 2\gamma\kappa_0^2 D_e\delta(t - t')$. In passing, we observe that the system encounters an effective Gaussian additive noise $\xi(t) [= F(t) + \pi(t)]$ and another noise which appears multiplicatively. The noises $\xi(t)$ and $\epsilon(t)$ are not statistically independent, their correlation may be expressed as $\langle \xi(t)\epsilon(t') \rangle = \langle \epsilon(t)\xi(t') \rangle = \beta(t - t')$ which one may calculate for a particular $\psi(t)$. Thus, the two mutually correlated noises appear in the dynamical equation of the open system. The appearance of cross-correlated noises has already been encountered while explaining various physical phenomena[30, 42, 43, 44]. Now, in terms of an auxiliary function $G(q)$ and a Gaussian stationary noise $R(t)$, the Langevin equation Eq.(28) can be written as

$$\ddot{q}(t) = -V'(q(t)) - \gamma p + G(q)R(t), \quad (31)$$

with

$$\langle \langle R(t) \rangle_e = 0 \quad \langle \langle R(t)R(t') \rangle \rangle = 2\delta(t - t'), \quad (32)$$

where $\langle \langle \dots \rangle \rangle$ implies average over the noise process $R(t)$ (this averaging over $R(t)$ consists of two independent averaging, one over thermal noise $F(T)$ and another over external noise $\epsilon(t)$). In Eq.(31),

$$G(q) = \left[(\gamma\kappa_B T + \gamma\kappa_0^2 D_e) + D_e\gamma^2\kappa_0^2 q^2 + 2\gamma\kappa_0 D_e q \right]^{1/2}. \quad (33)$$

Clearly, Eq.(30) along with Eq.(31), is not the FDR but serves as the thermodynamic consistency relation.

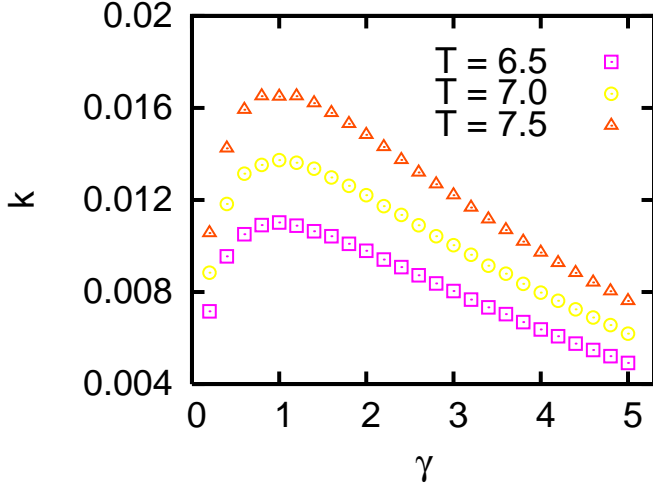


Figure 2: Change of the transition rate, k (sec^{-1}) with the dissipation constant, γ (sec^{-1}) for various temperatures in conjunction with $k_B=1$, $A=3.0$, $B=0.1$ $\kappa_0=0.05$, and $D_e=5.0$.

We now proceed to examine the noise induced transport. To do this, we numerically solve the Langevin equation, Eq.(28) [considering only quadratic bath-noise coupling, $g(x_j) = bx_j^2$], by the method developed by Sancho *et al.* for multiplicative noise and routinely calculate the MFPT[45], the inverse of which gives the escape rate from the metastable potential well. In our numerical implementation, we consider a double well potential of the form:

$$V(q) = -\frac{A}{2}q^2 + \frac{B}{4}q^4, \quad -\infty < q < +\infty$$

In Figure 2, we have plotted the rate k , obtained from Langevin simulation using the concept of mean first passage time, as a function of dissipation constant(γ) for various temperatures. For small γ , we observe that the rate increases with increase in γ whereas, for moderate to large γ , k decreases: the rates turnover with the (microscopic) friction (Figure 2). This observation can be explained with the help of the fact that the interaction between the system (say reactants) and the bath must transfer sufficient energy to activate the reactants above the energy barrier leading to products. The corresponding rate should therefore increase with the coupling represented by friction. An increase in friction, however, also slows down the reactants and induces a competing mechanism that reduces the rate. Thus the topology of the variation of k with dissipation constant in the present work also exhibits a typical signature of Kramers turnover. It is thus important to note that the simulation of the barrier crossing dynamics of the external noise-driven-reservoir-modulated dynamics of the system captures the essential turnover features of the Kramers dynamics of the closed system. In the detailed balance principle, when instead of additive internal thermal noise (for which FDR exists), the system encounters another multiplicative nonthermal noise that originates due to the modulation of the bath by an external noise, one recovers Kramers turnover nature. Thus, the

recovery of Kramers turnover for an thermodynamically open system is the key issue of our present investigation. Figure 2 also shows that for a given value of γ , the escape rate increases with increase in the temperature, as it should be. With increasing temperature, the sharpness of the turnover of the escape rate also increases.

To this end we would like to mention the works of Zhou[46] and Kalmykov *et al.*[47]. In both of the works, the authors have considered the standard Langevin equation with constant and additive δ -correlated white noise which relates with the dissipation by means of FDR (and hence describe thermodynamically closed system). In the work of Zhou[46], the Langevin equation was solved numerically to study the nature of the barrier dynamics, whereas the matrix-continued fraction method has been exploited to examine the thermally activated escape from a double-well potential for all values of dissipation by Kalmykov *et al.*[47]. In both the works, inevitable Kramers turnover was examined and compared with those obtained by the Mel'nikov and Meshkov method[48]. On the other hand, our present work deals with Kramers turnover in the case of open system in conjunction with both additive and multiplicative noises.

4. Summarizing Remarks

Many physical processes (with arbitrary complexity) influenced by the surroundings can be modeled as a potential barrier crossing event. Kramers showed that there is a qualitative difference in the barrier crossing dynamics at the low and high friction limits. Many authors have devised theoretical and computational models to describe the Kramers turnover by extending the basic assumptions found in the original Kramers work. The open question to be addressed here is whether the Kramers turnover is realizable in that class of thermodynamically open systems when the reservoir is modulated nonlinearly by an external noise and hence is relevant to chemical dynamics, in conjunction with other physical processes.

This work is a continuation of our studies on the models to describe the Kramers turnover. In Ref. [49], Ray Chaudhuri *et al.* shown numerically that the well known Kramers turnover phenomena is restored when the bath is *linearly modulated* by an external noise. However, in the present work the bath is being driven *nonlinearly* by an external noise. In this case, in spite of having a linear system-bath interaction, the nonthermal noise will appear multiplicatively in the Langevin equation. The origin of this multiplicative nature lies in the nonlinear driving of the bath itself. We have also envisaged the Kramers turnover phenomenon for the present model. Main results of this work are presented in Figure 2 which show the behavior of the rate constant as functions of the friction coefficient of the environment. From the aforesaid, we are led to the conclusion that irrespective of the mode in which the bath nonequilibrium takes place, the turnover phenomenon will make its appearance, and it is not only the additive noise that leads to such an observation, but also the multiplicative noise too has the potential to induce turnover. The observations of the present work are valid for all types of processes in which a classical system in contact with

a thermal heat bath is driven out of equilibrium by classical, generally time-dependent fluctuating forces.

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